

# Chemical Force Microscopy Research at the National Institute of Standards and Technology

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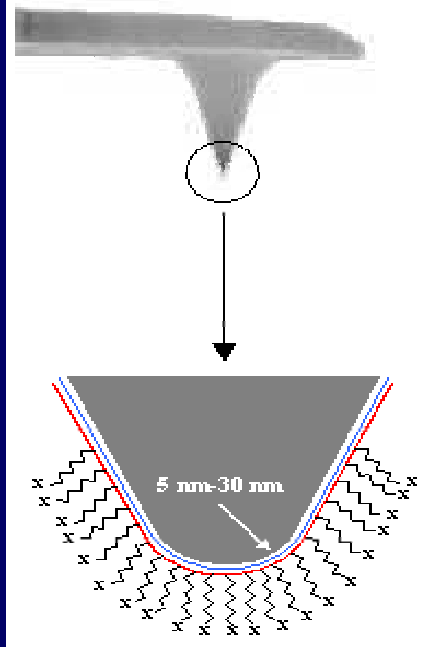
Optical Technology Division

*Physics Laboratory*

# Chemical Force Microscopy (CFM)

C.D. Frisbie, L.F. Rozsnyai, A Noy, M.S. Wrighton, C.M. Lieber, 1994, *Science* 265:2071

A. Noy, D.V. Vezenov, and C.M. Lieber, *Annu. Rev. Mater. Sci*, 1997, 27:381



Au coated AFM  
Probe, treated with  
thiol SAM

***Chemically Functionalized AFM probe with increased sensitivity to chemical differences:***

- *Tapping-Mode Phase imaging*
- *Friction Force Contact imaging*

**The promise of CFM:**

nm scale chemical imaging of complex specimen surfaces

- *Multiphase Polymers*
- *Biological Samples*

**Barriers to a Better CFM:**

Moving CFM beyond the demonstration stage:

- Characterization of probe functionalization
  - *Quality and Reliability of SAM*
- Relation of CFM contrast to traditional chemical analysis
- Lack of **Challenging** Model Specimens

# The NIST CFM Project:

*Funded by the NIST Advanced Technology Program*

## Highly Designed Reference Specimens

Polymers Division, MSEL

- Soft Lithography
- Self Assembly
- Gradient Approach

## Contrast Enhancement Strategies

Mat. & Bldg. Res. Div, BFRL

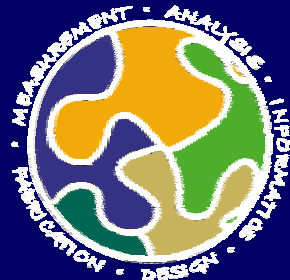
- Traditional and CNT Probe functionalization
- Humidity enhanced CFM contrast

**CFM**

## Probe Characterization

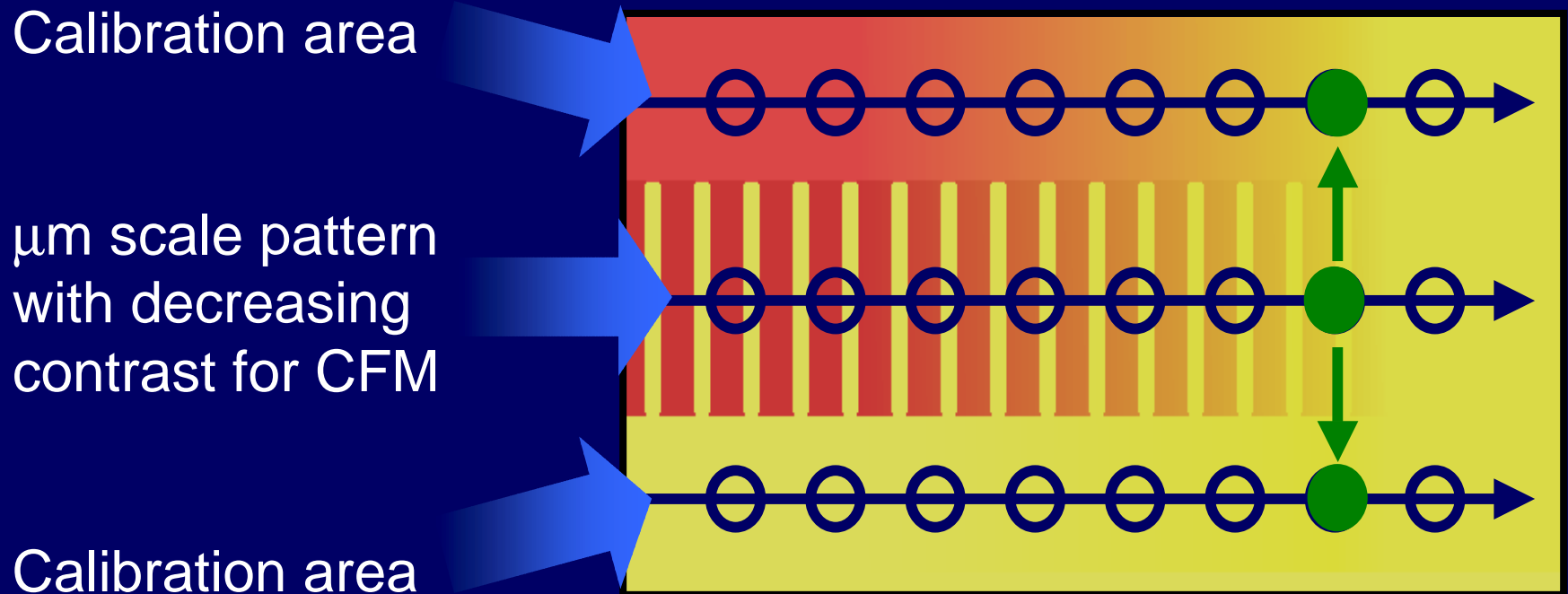
Optical Technology Division, PL

- Advanced Spectroscopy
  - Sum frequency generation
- Fluorescence Imaging
- Traditional and CNT probes



# Gradient Reference Specimen for CFM

Fasolka, Karim – Polymers Division, MSEL



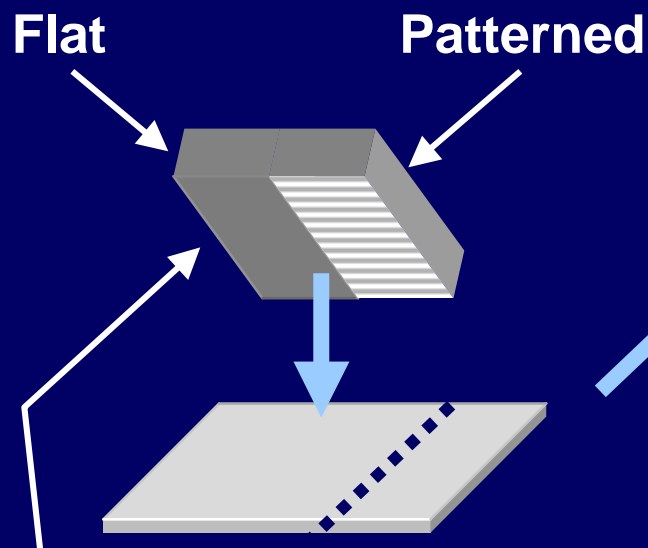
- **Hydrophobic** and **Hydrophilic** domains
- Illuminates **chemical sensitivity** (min. contrast)
- Relates contrast to traditional measurements (calibration) e.g. FTIR, contact angle
- “Gradually challenges” CFM technique

# Fabrication of Reference Specimen

## ① $\mu$ -contact print thiol SAMs on Au substrate

### Print step

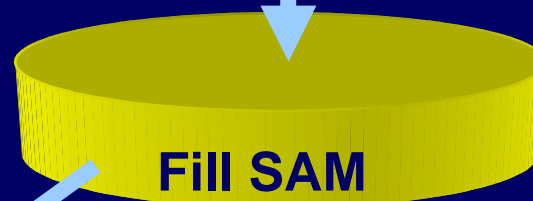
Composite PDMS Stamp



Print **SAM**

### Fill step

Complimentary **SAM** solution



Interdigitated  
SAMS



### Thiol SAMs

- $(\text{CH}_2)_{15}\text{-COOH}$
- $(\text{CH}_2)_{17}\text{-CH}_3$

# Fabrication of Reference Specimen

## ② Application of UV-ozone exposure gradient

Translation stage:  $v=a(t)$

Slit aperture

- 192nm UV wand source
- $O_3$  and O generation

Exposure dependent SAM conversion

$-(CH_2)_{17}-CH_3 \longrightarrow$  O-containing species

hydrophobic

hydrophilic

2  $\mu m$  lines  
18  $\mu m$  pitch

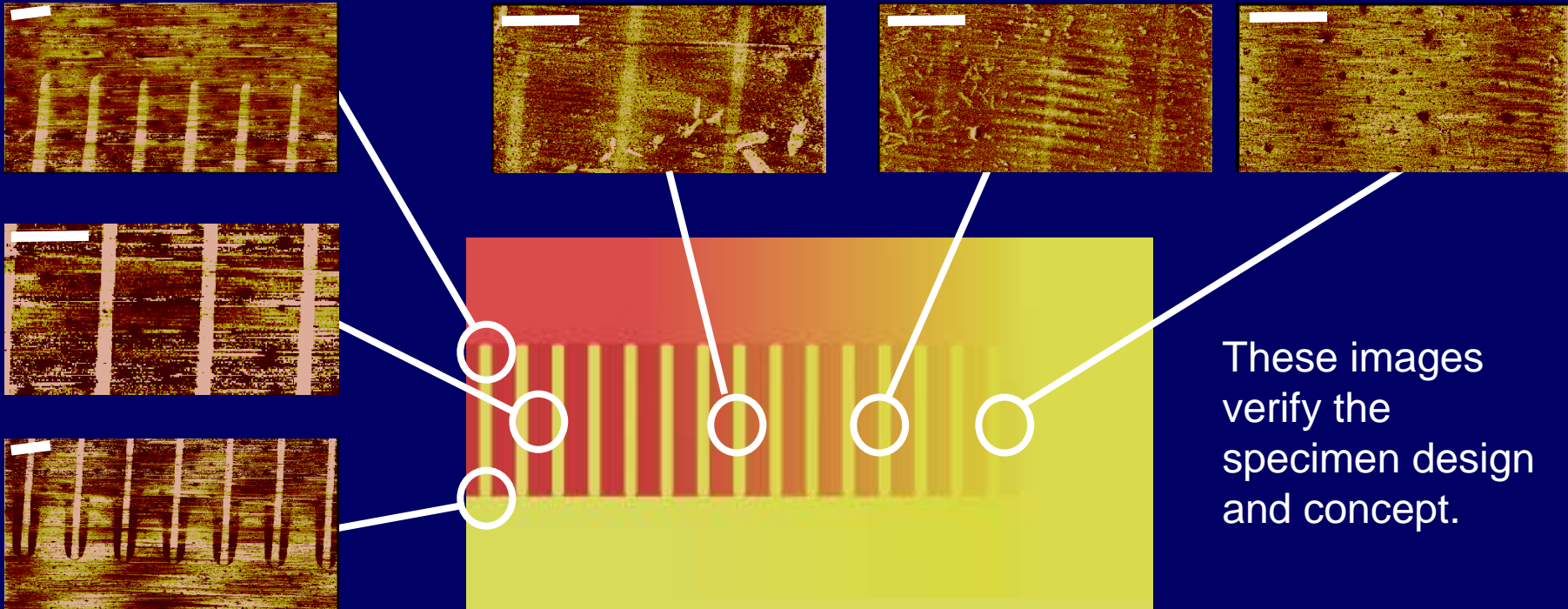
hydrophilic

15 mm

# Gradient Reference Specimen Demonstration

Contact-Mode Friction AFM Images

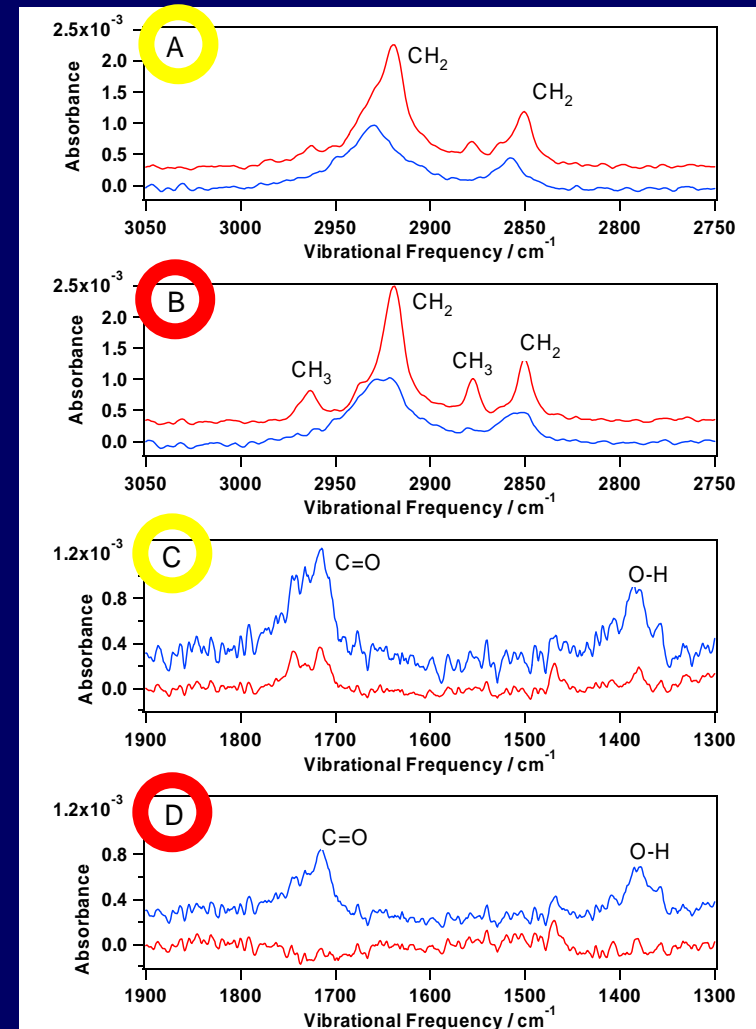
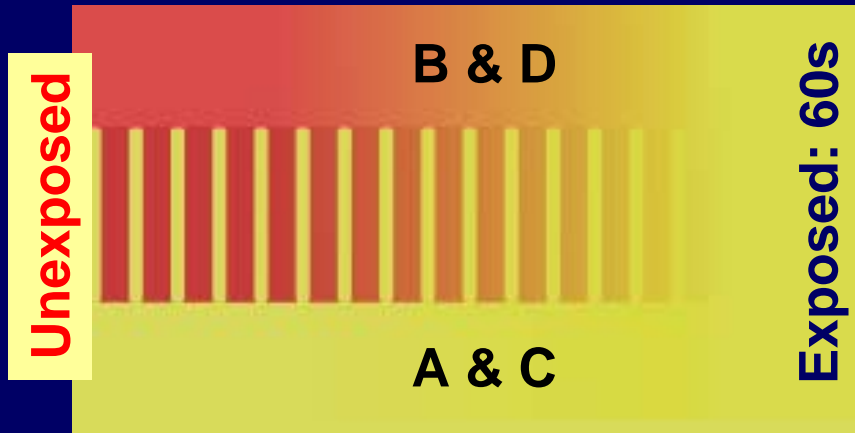
Scale bars are 10 $\mu$ m  
Images have equal z-scales



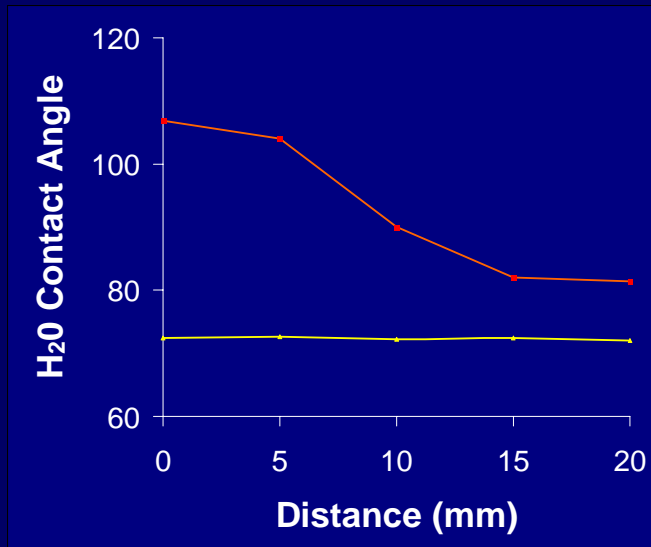
Print: CH<sub>3</sub> Terminated SAM  
Fill: COOH Terminated SAM

Linear Exposure Ramp: 0 - 60s

# Reference Specimen Characterization/Calibration



## Water Contact Angle Measurements



Reflection-Absorption Infrared Spectroscopy (K.A. Briggman)

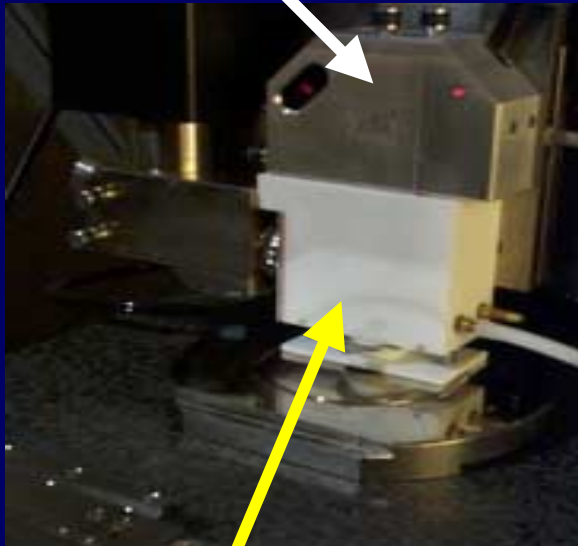


# Relative Humidity (RH) Enhanced CFM Contrast

T. Nguyen, X. Gu, M. VanLandingham - BFRL

## AFM w/ RH Control

AFM scan head

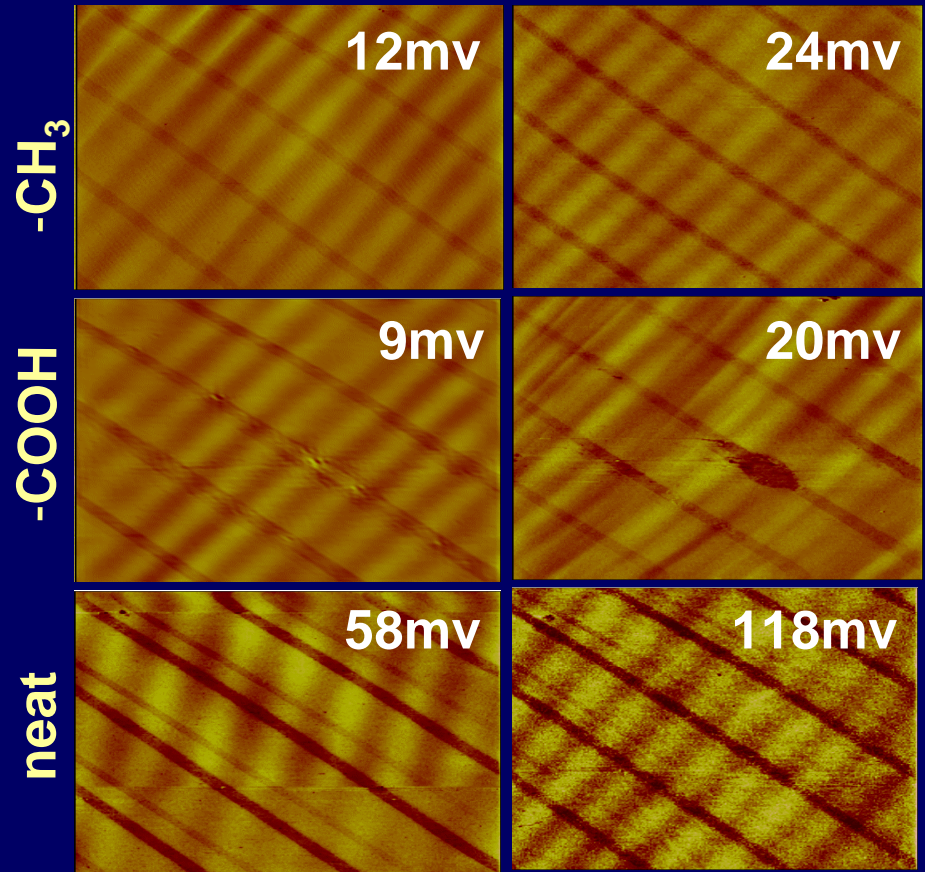


Humidity chamber

To RH control

8% RH

93% RH



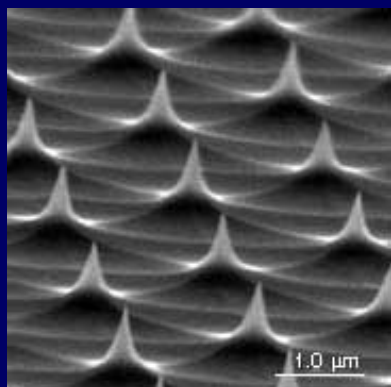
Friction CFM for three probe types  
-COOH Print, -CH<sub>3</sub> Fill, 18μm pitch

# CFM Probe Characterization

K.A. Briggman, J. Hwang – Physics Lab

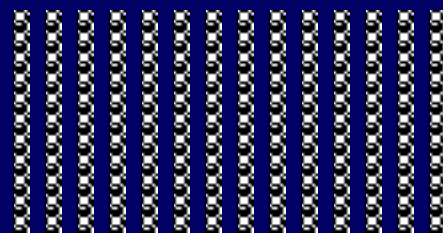
*Gauging the quality of probe functionalization*

Ultrasharp tip  
arrays



Silicon-MDT Ltd.  
[www.siliconmdt.com](http://www.siliconmdt.com)

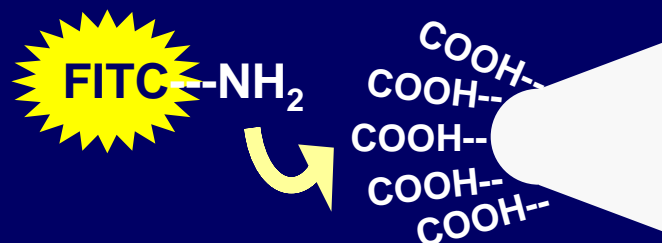
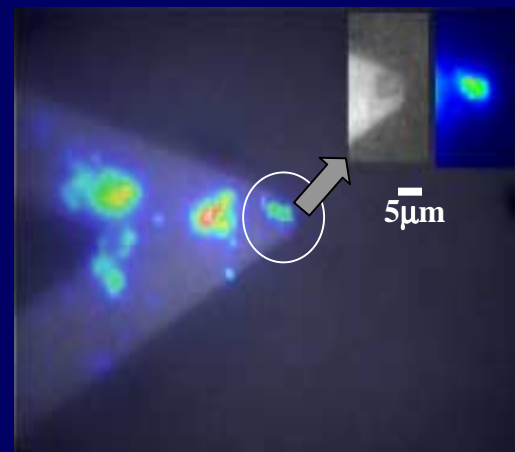
CVD-grown  
CNT Brush



Substrate/Catalyst

Prof. Eric A. Grulke  
University of Kentucky

Fluorescence imaging  
of tip functionalization



## Surface-Sensitive IR Spectroscopies

- Reflection-absorption IR Spectroscopy
- Sum Frequency Generation Spectroscopy

# Future Directions

- Increasingly complex reference specimens
  - Chemical *and* Topographic Patterning
  - Block Copolymer Fracture Surfaces
- Refinement of RH-contrast enhancement
  - Stability improved, Mechanism Explored
- Further Development of Probe Characterization Methods
  - Probe-like array surfaces
  - Spectroscopic and Imaging Techniques

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## Acknowledgements

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